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Applications of hydrogen-bond-acceptor templates to direct 'in-phase' reactivity of a diene diacid in the solid state

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Supplementary data

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Materials:

(*E*,*E*)-2,5-dimethylmuconic acid (98%, Alfa Aesar), methanol (ACS reagent, ≥ 99.8%, Sigma-Aldrich), ethyl acetate (ACS reagent, ≥ 99.5%, Sigma-Aldrich), and hexanes (ACS reagent, ≥ 99.5%, Sigma-Aldrich) were used as received. Hydrogen-bond acceptor templates 1,8-dpn and 2,3-nap were prepared according to the literature procedures.[5,6]

Methods:

NMR Studies

All products were characterized by the Avance-400 and Avance-600 Bruker NMR spectrometers (Billerica, MA) operating at 400 and 600 MHz, respectively, using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent. ^1H and ^{13}C chemical shifts were referenced with the residual proton and carbon chemical shifts of the solvents (DMSO-d_6, ^1H, 2.5 ppm; $_{13}C$, 39.5 ppm). Fractions with milligram quantities of the product were characterized with a battery of one- and two-dimensional heteronuclear experiments [^1H, 1D correlated spectroscopy (COSY), and heteronuclear multiple bond correlation (HMBC)]. Gradient-assisted versions of the pulse sequences. Inverse detection were used for these 2D experiments. Typical parameters for the NMR experiments were as follows: ^1H (TD, 64k; NS, 4k), ^{13}C (TD, 128k; NS, 10000), 1D COSY (TD, 64k; NS, 512), and ^{13}C-^1H HMBC (TD, 2k; TD1, 128; NS, 32; DS, 128). TD, NS, and DS refer to time domain data points, number of scans, and dummy scans, respectively. All of the NMR data were processed with TOPSPIN 1.3 suite of software programs. One-dimensional ^1H data were processed with zero-filling to 64k data points and 0.2 Hz exponential line broadening, whereas ^{13}C spectra were processed with zero-filling to 128k data points and 1.0 Hz of exponential line broadening. The 2D NMR data were processed with the zero-filling to 2048 points and 1024 points in acquisition and second dimension, respectively. Relative numbers of proton signals multiplied by the integral areas were used for the quantification.

Single-crystal X-ray Diffraction

Single-crystal X-ray diffraction studies of (2,3-nap)·(dmma), (1,8-dpn)·(dmma), and (1,8-dpn)·(cbda) were performed on a Nonius Kappa CCD diffractometer. Data collection was conducted at 150 K using MoK$_\alpha$ radiation (λ = 0.71073 Å). A total of 491 diffraction images were collected in two phi scans (frame-exposure times: 60 s and 240 s) and four omega scans (frame-exposure times: 240 s) with 2.0º per-frame rotations. Data reduction was accomplished using the *HKL Denzo* and *HKL Scalepack* programs (Otwinowski & Minor, 1997). The structure was fully solved *via* direct methods using *SHELXS-97* (Sheldrick, 2008). Refinement by full-matrix least-squares based on F_2 was performed utilizing *SHELXL-97* (Sheldrick, 2008). All hydrogen atoms were refined in geometrically constrained riding positions.

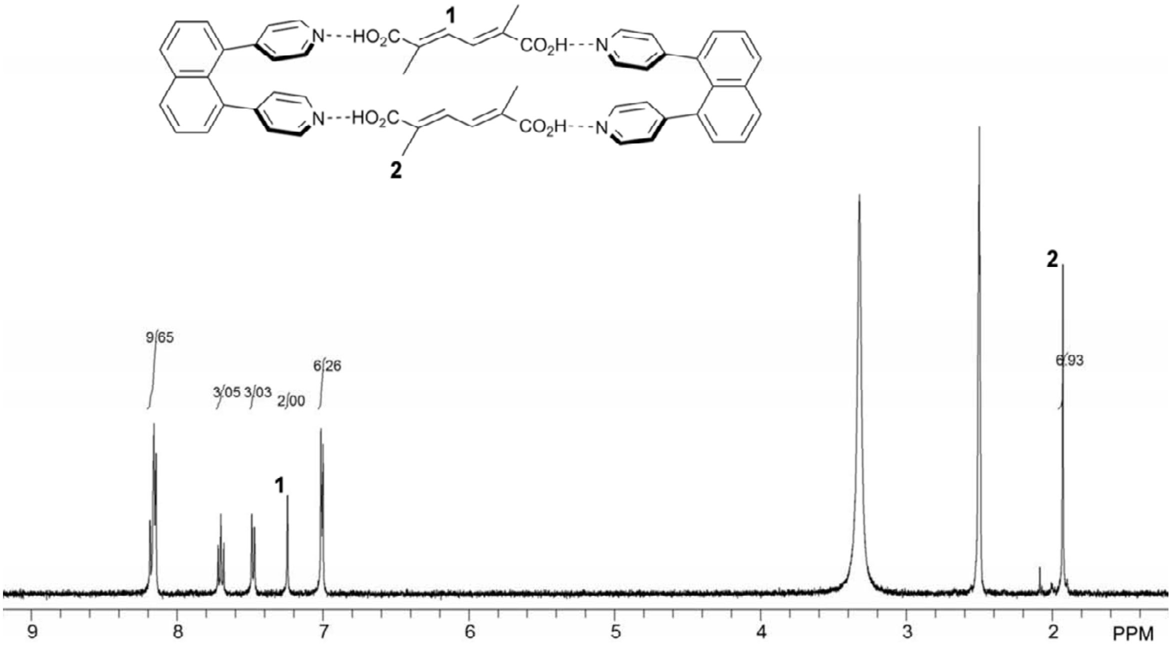


Figure S1. ^{1}H NMR spectrum of co-crystal (1,8-dpn)·(dmma) before photoreaction

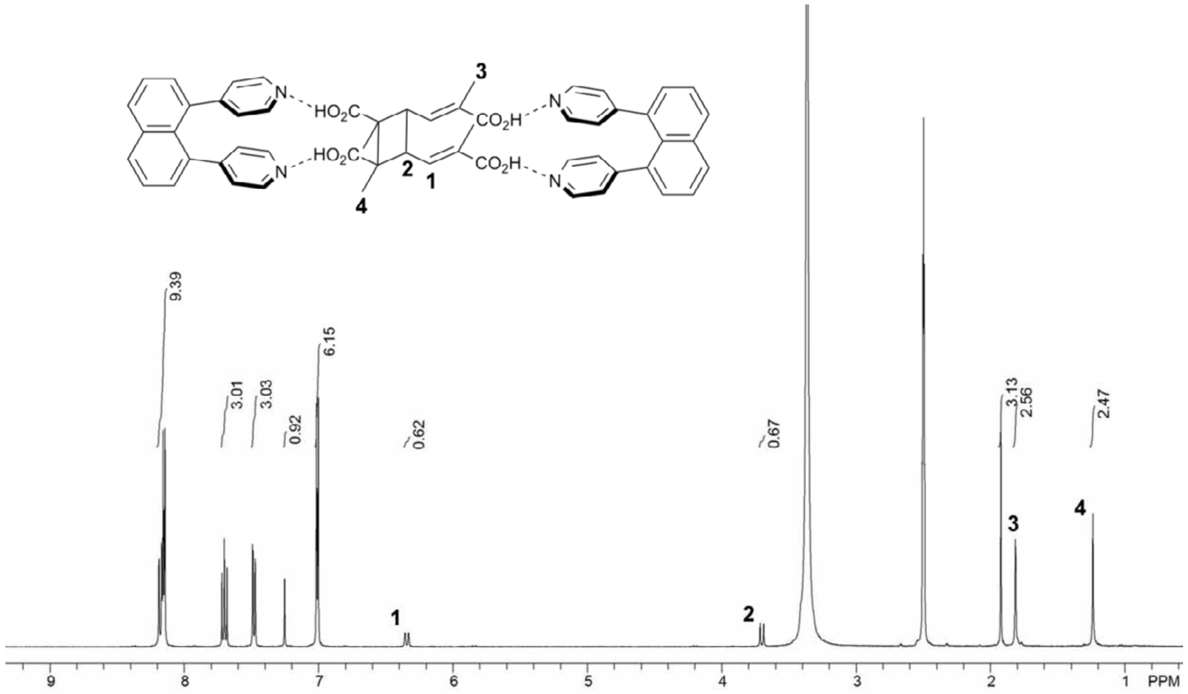
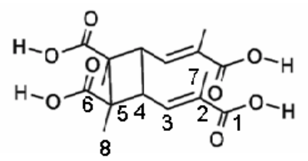


Figure S2. ^{1}H NMR spectrum of co-crystal (1,8-dpn)·(dmma) after photoreaction

Table S1. ^{1}H and ^{13}C chemical shifts of cbta.



	^{1}H	^{13}C
1		170.0
2		132.0*
3	6.03	131.8
4	3.39	43.8
5		*
6		*
7	1.78	20.2
8	1.26	28.3

*Either tentative or cannot be assigned due to resonance overlap or lack of HMBC correlations.